РОЗДІЛ II
Неорганічна та фізична хімія

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The Cu$_2$Se–PbSe–SiSe$_2$ System and the Crystal Structure of CuPb$_{1,5}$SiSe$_4$

Isothermal section of the Cu$_2$Se–PbSe–SiSe$_2$ system at room temperature was investigated by X-ray diffraction. The existence of the quaternary compound was confirmed, and its composition was ascertained as CuPb$_{1,5}$SiSe$_4$. The crystal structure of CuPb$_{1,5}$SiSe$_4$ was refined by X-ray powder method (space group $I\bar{4}3d$, $a = 1,43386$ nm, $R_I = 0,0834$).

Keywords: Isothermal Section, Crystal Structure, Chalcogenides.

Setting and importance of the scientific problem. The principal task of modern semiconductor materials science is the creation and investigation of new materials, both for the traditional technologies and for revolutionary new applications. Taking into account the increase of the needs of modern electronics and the limitations of the properties of functional materials, the researchers investigate new ternary and more complex inorganic compounds.

This paper on the Cu$_2$Se–PbSe–SiSe$_2$ system is a part of the comprehensive investigation of the A$^I_2$X–PbX–D^{IV}X$_2$ systems (A^I = Cu, Ag; D^{IV} = Si, Ge, Sn; X = S, Se). Character of the chemical interaction of components in other systems of this type, phase equilibria and quaternary compounds that form in the systems are described in [8].

The study of the crystal structure, physico-chemical and physical properties of ternary and quaternary phases permits us to use them in further investigations, in development and prediction of the fields of their application.

Presented paper is of interest for the search of new compounds for semiconductor materials science and for the tuning of the physical properties by the substitution of elements within Ba$_3$CdSn$_2$S$_8$/Eu$_{1,75}$Ag$_{0,5}$GeS$_4$ structure type.

Analysis of recent studies. According to literature reports [2; 9] the Cu$_2$Se–SiSe$_2$ system features ternary compounds Cu$_2$SiSe$_3$ and Cu$_8$SiSe$_6$. The crystal structure of Cu$_2$SiSe$_3$ was determined in [9] as the monoclinic space group (S. G.) Cc, $a = 1,121$, $b = 0,562$, $c = 0,861$ nm, $\beta = 99°$ [9]. The phase diagram of the Cu$_2$Se–SiSe$_2$ system according to [6] is presented in Fig. 1.

The section is quasi-binary in the ternary system Cu–Si–Se. Cu$_2$SiSe$_3$ melts incongruently at 1190 K, while Cu$_8$SiSe$_6$ melts congruently at 1380 K. Both compounds have polymorphous transitions, at 890 K (Cu$_2$SiSe$_3$) and 335 K (Cu$_8$SiSe$_6$). The eutectic point coordinates are 1275 K and 90 mol.% Cu$_2$Se, 1155 K and 40 mol.% Cu$_2$Se, the peritectic point lies at 1190 K and 47 mol.% Cu$_2$Se. The eutectoid decomposition of the solid solutions of high-temperature modification of Cu$_2$Se takes place at 413 K. Low-temperature modification of Cu$_8$SiSe$_6$ crystallizes in the orthorhombic S. G. $Pmn2_1$ with the lattice periods $a = 0,72835$, $b = 0,72185$, $c = 1,02281$ nm.

Phase diagram of the Cu$_2$Se–PbSe system that is presented in Fig. 1 was investigated using DTA results in [4]. The eutectic reaction L $\leftrightarrow$ β-Cu$_2$Se + PbSe takes place at 888 K and corresponds to 46 mol.% PbSe. Phase transition of copper selenide caused the peritectoid reaction β-Cu$_2$Se + PbSe $\leftrightarrow$ α-Cu$_2$Se that takes place at 420 K.

Phase diagram of the SiSe₂–PbSe system was not constructed. Ternary compound Pb_2SiSe_4 forms upon melting $SiSe_2$ and $PbSe$ in the ratio of 1:2 [3]. X-ray structure investigation showed that Pb_2SiSe_4 crystallizes in the monoclinic S.G. $P2_1/c$. The unit cell parameters are $a = 0,85670$, $b = 0,70745$, $c = 1,36160$ nm, $\beta = 108,355°$.
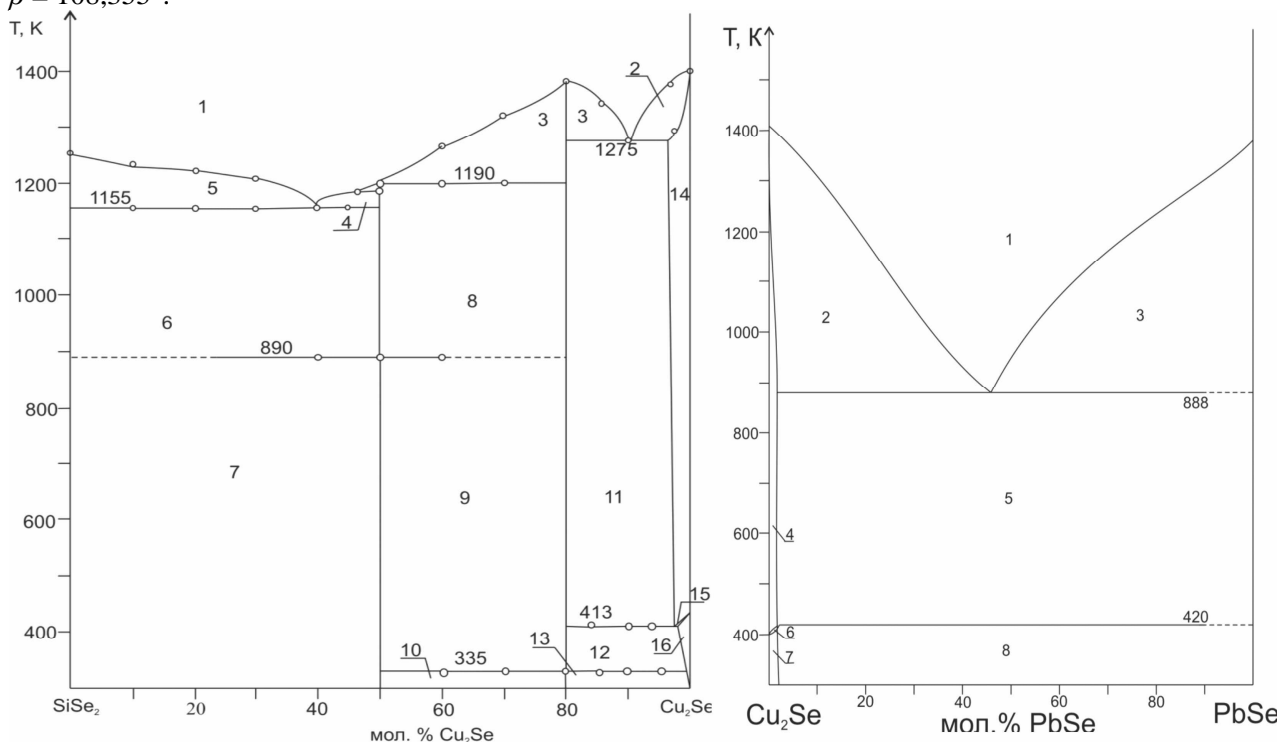
Fig. 1.* Phase diagrams of the Cu₂Se–SiSe₂ system (left): 1 – L, 2 – L + α, 3 – L + β-Cu₈SiSe₆, 4 – L + γ-Cu₂SiSe₃, 5 – L + SiSe₂, 6 – γ-Cu₂SiSe₃ + SiSe₂, 7 – γ′-Cu₂SiSe₃ + SiSe₂, 8 – γ-Cu₂SiSe₃ + β-Cu₈SiSe₆, 9 – γ′-Cu₂SiSe₂ + β-Cu₈SiSe₆, 10 – γ′-Cu₂SiSe₃ + β′-Cu₈SiSe₆, 11 – β-Cu₈SiSe₆ + α, 12 – β-Cu₈SiSe₆ + α′, 13 – β′-Cu₈SiSe₆ + α′, 14 – α, 15 – α + α′, 16 – α′; and of the Cu₂Se–PbSe system (right): 1 – L, 2 – α-Cu₂Se +L, 3 – L + PbSe, 4 – α-Cu₂Se, 5 – α-Cu₂Se + PbSe, 6 – α-Cu₂Se + β-Cu₂Se, 7 – β-Cu₂Se, 8 – β-Cu₂Se + PbSe

The existence of a quaternary compound in the Cu_2Se–$PbSe$–$SiSe_2$ system is reported in [1], its composition was given as $Cu_{0,5}Pb_{1,75}SiSe_4$. Obtained sample of this composition was not single-phase. The presence of Pb_2SiSe_4 as the impurity phase was determined. The complete investigation of the crystal structure of $Cu_{0,5}Pb_{1,75}SiSe_4$ was not performed. The lattice parameters was determined as $a = 1,4345$ nm, S.G. $I\bar{4}3d$, $Eu_{1,75}Ag_{0,5}GeS_4$ structure type.

Objective and Goals. The objective and goals of the work were the study of the phase equilibria in the Cu_2Se–$PbSe$–$SiSe_2$ system, the investigation of its isothermal section, ascertaining the composition and determining the crystal structure of the quaternary compound that forms in the system.

Materials and Methods. Isothermal section of the Cu_2Se–$PbSe$–$SiSe_2$ system was investigated on 20 alloys. The alloys of 1 g mass each were synthesized from high-purity elements (copper, 99,999 wt.%, silicon, 99,999 %, selenium, 99,999 %, lead, 99,99 %) in evacuated to 0,1 Pa quartz containers. Quartz ampoules were placed in a shaft-type furnace and heated to 870 K at the rate of 40 K/hr. They were kept at this temperature for 24 hrs for the complete bonding of selenium, then heated at the rate of 15–20 K/hr to 1270 K and kept for 12 hrs for the completion of the reaction with silicon. The alloys were cooled at the rate of 20 K/hr to 670 K where they were annealed for 500 hrs. The final stage was the cooling to room temperature.

X-ray phase analysis was used for the determination of the phase composition of alloys for the construction of the isothermal section. The diffraction patterns were recorded at a DRON 4-13 diffractometer (CuK$_\alpha$ radiation) in the *2θ* range from 10 to 80° with scan step 0,05° and the exposure of 3 s (depending on typical peak intensity). The comparison standards were the powder patterns of binary and ternary compounds.

The diffraction pattern for the refinement of the crystal structure of the quaternary compound was recorded in the 2θ range from 10 to 100º with scan step 0,05º and the exposure of 20 s in each point. The computation was performed by Rietveld method using WinCSD software package [10].

Results. Isothermal section of the system at room temperature studied by the results of the investigation of 20 alloys is presented in Fig. 2. X-ray phase analysis confirmed the presence of the ternary compounds Cu_8SiSe_6, Cu_2SiSe_3 and Pb_2SiSe_4.
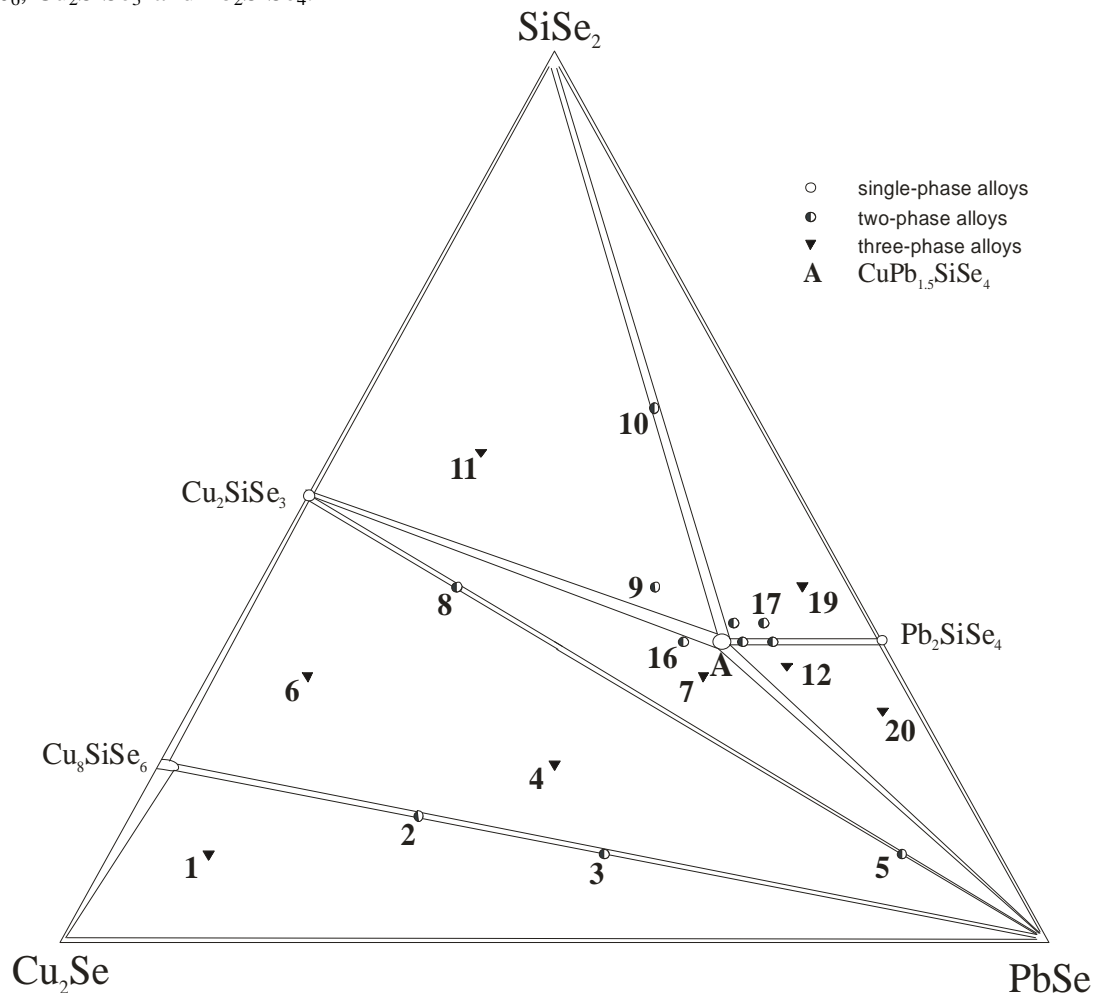
Fig. 2. **Isothermal section of the Cu_2Se–$PbSe$–$SiSe_2$ system at 300 К**

Seven alloys in a cluster near point A (№ 12 to 18 in Fig. 2; not all alloys are identified by number for simplicity) were synthesized to ascertain the composition of the quaternary phase. It was established that the best diffraction pattern corresponds to the composition of $CuPb_{1,5}SiSe_4$.

The position of six three-phase fields was determined, namely Cu_2Se–Cu_8SiSe_6–$PbSe$, Cu_8SiSe_6–Cu_2SiSe_3–$PbSe$, Cu_2SiSe_3–$CuPb_{1,5}SiSe_4$–$PbSe$, $CuPb_{1,5}SiSe_4$–Pb_2SeSe_4–$PbSe$, $CuPb_{1,5}SiSe_4$–Pb_2SiSe_4–$SiSe_2$, and Cu_2SiSe_3–$CuPb_{1,5}SiSe_4$–$SiSe_2$. Twelve two-phase equilibria between binary, ternary and quaternary compounds were identified.

The diffraction patterns of the synthesized alloys are plotted in Fig. 3, and the diffraction patterns of alloys prepared for the refinement of the composition of the quaternary compound are presented in Fig. 4.

The details of the computation of the $CuPb_{1,5}SiSe_4$ structure are given in Table 1. This compound crystallizes in the cubic structure, space group $I\bar{4}3d$, and contains 16 formula units per unit cell. The lattice constant a = 1,43378 nm, the volume of the unit cell is 2,9474 nm^3. Fractional atomic coordinates and equivalent isotropic temperature displacement parameters in the $CuPb_{1,5}SiSe_4$ structure are given in Table 2, bond distances and coordination numbers of atoms are listed in Table 3. Experimental and calculated diffraction patterns of the $CuPb_{1,5}SiSe_4$ sample and their difference are plotted in Fig. 5.
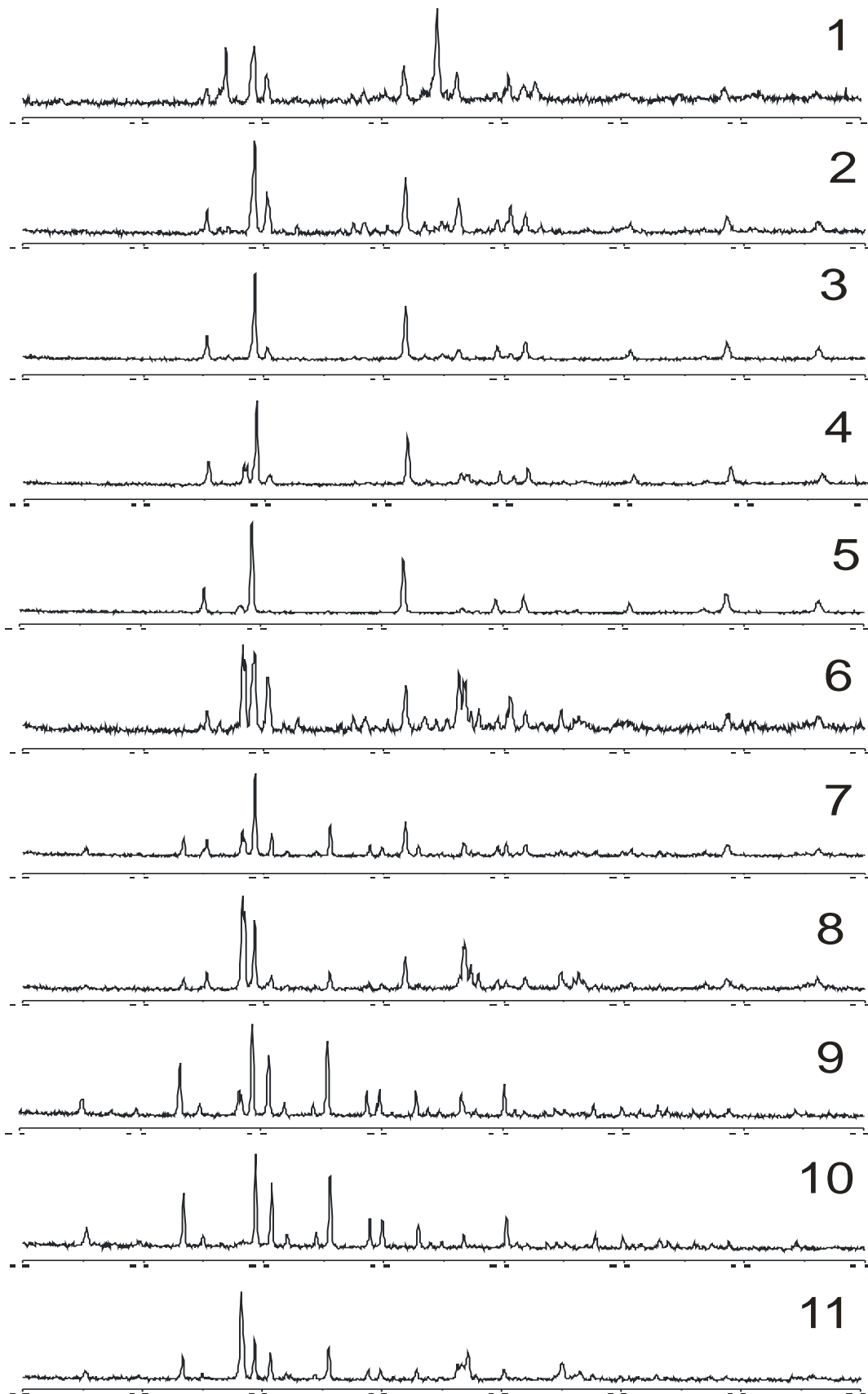
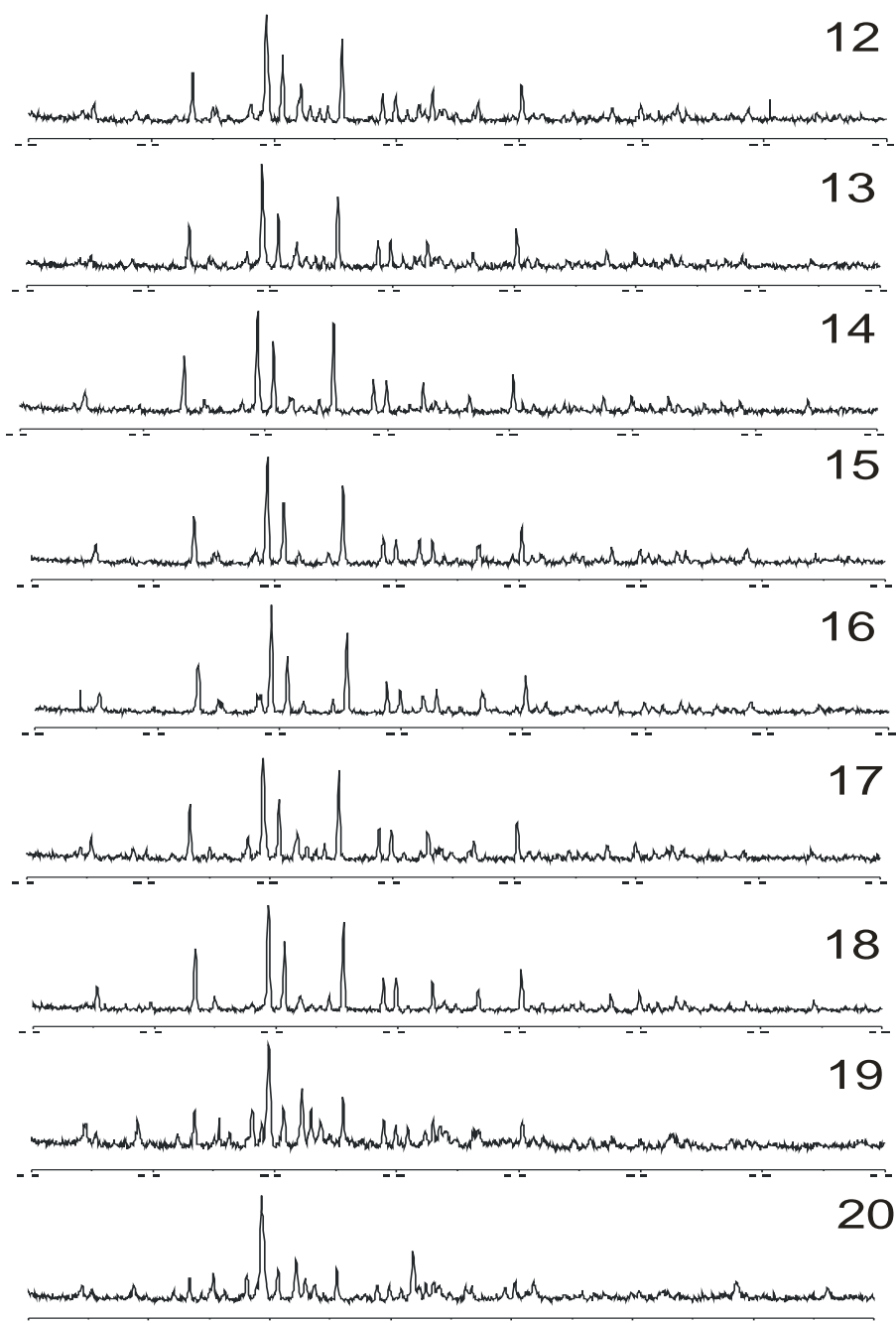*Fig. 3.* Diffraction patterns of the synthesized alloys

Fig. 4. Diffraction patterns of the alloys for the refinement of the composition of the quaternary compound

Table 1

Results of the refinement of the CuPb$_{1,5}$SiSe$_4$ crystal structure

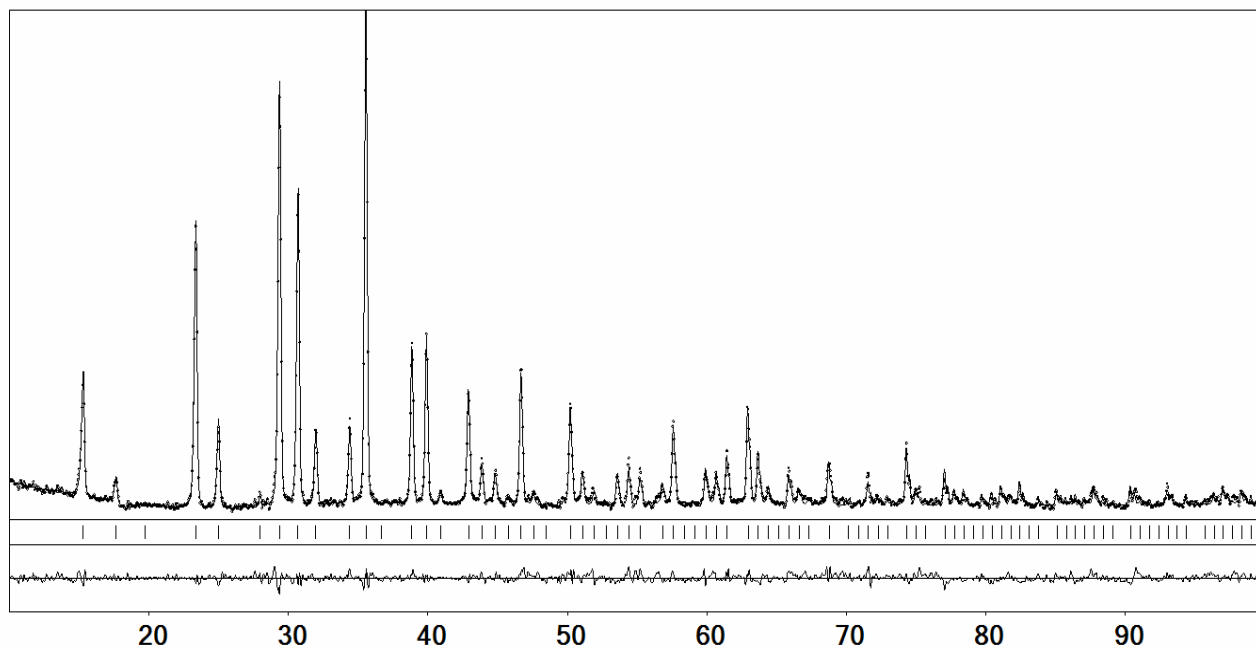| Compound	Ag$_2$GeS$_3$
Pearson symbol	*cI140*
Space group	*I*-43*d* (№ 220)
Number of formula units per unit cell	16
Lattice parameter *a* (*nm*)	1,43378(6)
Cell volume (*nm*^{3})	2,9474(4)
Calculated density (*g/cm*^{3})	6,4738(8)
Fit factors R_I and R_P	0,0873 and 0,1628

***Fig. 5.* Experimental (dotted line) and calculated (solid line) diffraction patterns for CuPb$_{1,5}$SiSe$_4$ and their difference (solid line below the plot). Vertical lines denote the position of hkl reflections of the compound**

Table 2

Fractional atomic coordinates, isotropic temperature displacement parameters and site occupation in the CuPb$_{1,5}$SiSe$_4$ structure

Atom	Wyckoff site	x/a	y/b	z/c	$B_{iso} \times 10^2$, nm^2
0,64(1) Cu1	12a	3/8	0	1/4	0,7(4)
0,344(7) Cu2	24d	0,2998(11)	0	1/4	2,0(7)
Pb	24d	0,0184(2)	0	1/4	1,43(8)
Si	16c	0,2162(7)	0,2162(7)	0,2162(7)	3,2(3)
Se2	16c	0,1092(3)	0,1092(3)	0,1092(3)	2,51(11)
Se1	48e	0,1395(3)	0,3287(3)	0,1842(3)	2,2(2)

Table 3

Inter-atomic distances (δ) and coordination numbers of atoms (C. N.) in the CuPb$_{1,5}$SiSe$_4$ structure

Atoms	δ, Å	C. N.	Atoms	δ, Å	C. N.
Cu1–4Se1	3,151(4)	4	**Se2**–1Si	2,657(11)	4
Cu2–2Se1	2,832(10)	4	–3Pb	2,868(4)	
–2Se1	3,108(4)		**Se1**–1Si	2,005(11)	
Pb–2Se2	2,868(4)	8	–1Cu2	2,832(10)	
–2Se1	3,214(4)		–1Cu2	3,108(4)	6
–2Se1	3,307(4)		or –1Cu1	3,151(4)	
–2Se1	3,470(4)		–1Pb	3,214(4)	
Si–3Se1	2,005(11)	4	–1Pb	3,307(4)	
–1Se2	2,657(11)		–1Pb	3,470(4)	

The location and the coordination polyhedra of atoms in the CuPb$_{1,5}$SiSe$_4$ structure are shown in Fig. 6. The polyhedra of Si, Cu$_1$, Cu$_2$ and Se$_2$ are tetrahedra with various degree of distortion; Se1 surrounding forms a distorted trigonal prism, the polyhedron for Pb is a distorted trigonal prism with two additional atoms across the side faces.

The structure of the $CuPb_{1,5}SiSe_4$ compound may be presented as a result of gradual isovalent substitution of silicon atoms in the $SiSe_2$ structure [9] with metallic component atoms according to the formula $Cu_yPb_xSi_{2-x/2-y/4}Se_4$. The intermediate compounds in such a substitution would be Pb_2SiSe_4 [3] and $Ag_{0,5}Pb_{1,75}GeSe_4$ [5] as shown in Fig. 7. For instance, Pb_2SiSe_4 is described as the substitution of lead atoms for one half of silicon atoms in the silicon diselenide structure where lead atoms tend to form layers in between the tetrahedra of selenium atoms centered by silicon atoms. Further substitution of silver atoms for 1/8 of lead atoms in the Pb_2SiSe_4 structure yields the $Ag_{0,5}Pb_{1,75}GeSe_4$ compound where metal atoms form chains in the space between the above-mentioned tetrahedra. The substitution of copper atoms for 1/4 of lead atoms in the Pb_2SiSe_4 structure results in the $CuPb_{1,5}SiSe_4$ compound where the increase of the ratio of cation atoms to anion atoms causes a small distortionary shift of the tetrahedra from the planes that they occupy.
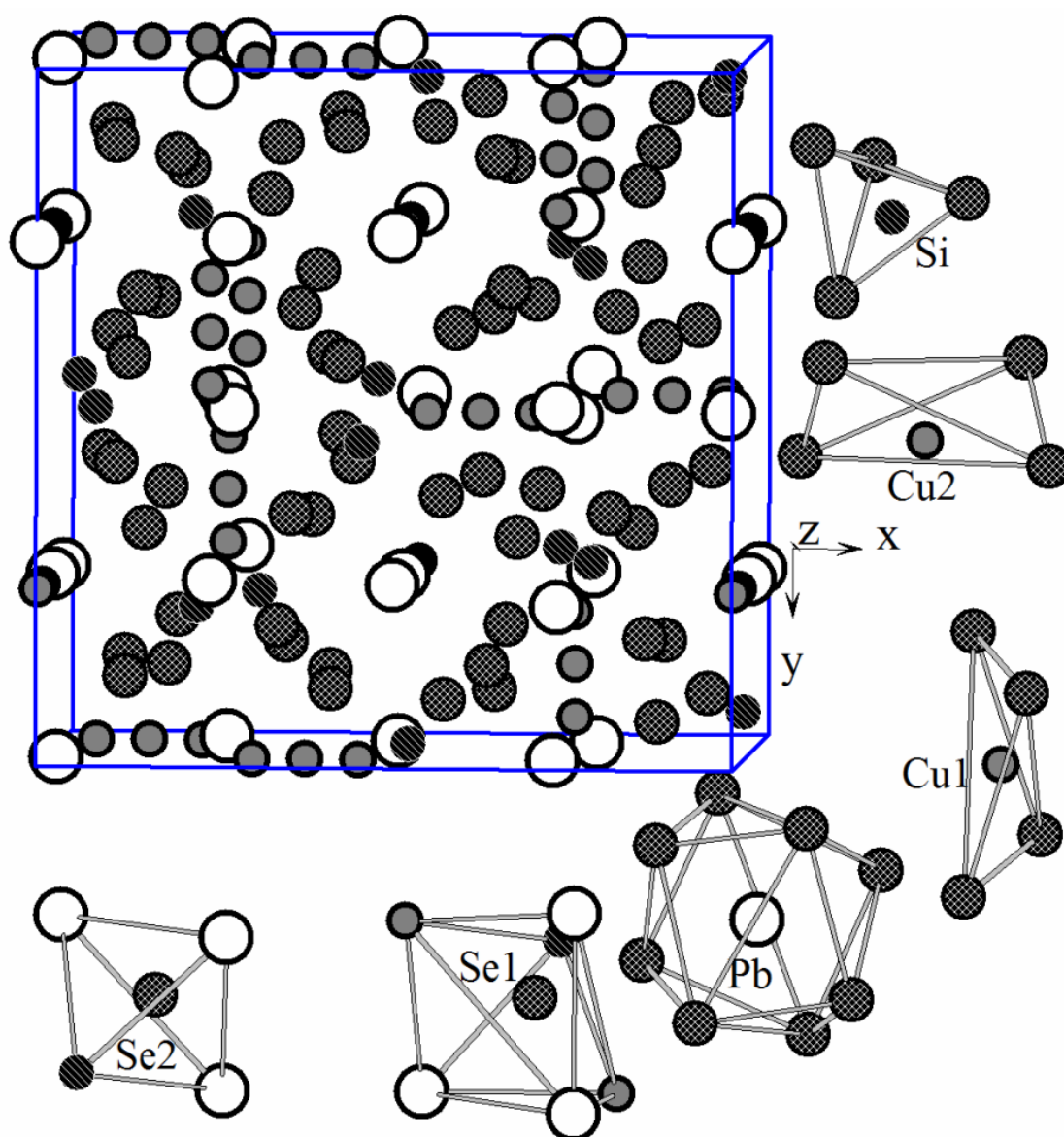

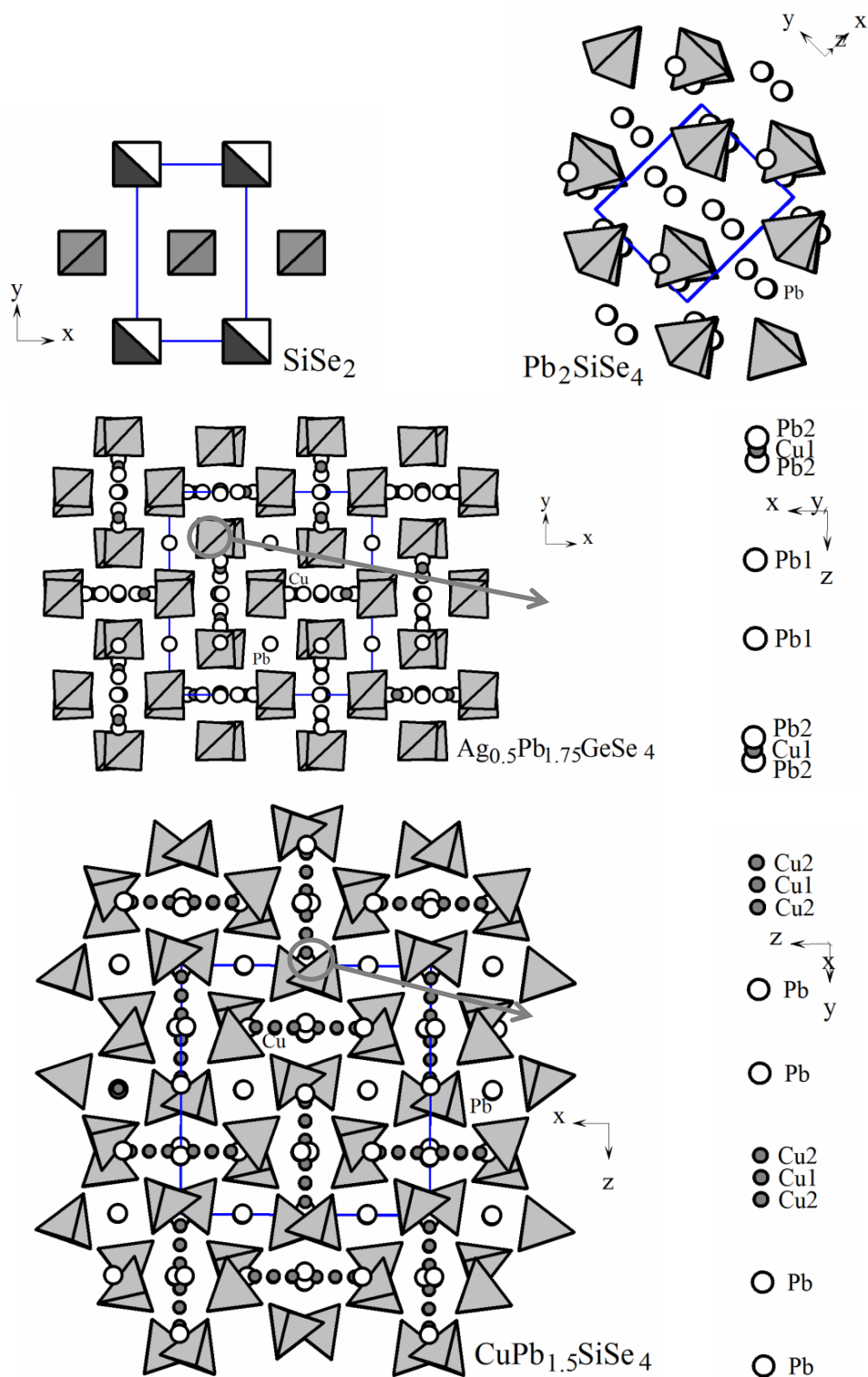*Fig. 6.* **Location and coordination polyhedra of atoms in the $CuPb_{1,5}SiSe_4$ structure**

Fig. 7. **Packing of metal component atoms in between the Si(Ge)Se₄ tetrahedra in the structures of SiSe₂, Pb₂SiSe₄, Ag₀,₅Pb₁,₇₅GeSe₄ and CuPb₁,₅SiSe₄**

Conclusions. Isothermal section of the quasi-ternary system at room temperature $Cu_2Se–PbSe–SiSe_2$ was investigated. Six three-phase fields and twelve two-phase equilibria were identified. The composition of the quaternary compound was defined as $CuPb_{1,5}SiSe_4$. The refinement of its crystal structure showed that the compound crystallizes in the cubic space group $I\overline{4}3d$, the lattice parameter $a = 1,43378$ nm. Genesis of the crystal structure in the series $SiSe_2 \rightarrow Pb_2SiSe_4 \rightarrow Ag_{0,5}Pb_{1,75}GeSe_4 \rightarrow CuPb_{1,5}SiSe_4$ is discussed.

Sources and literature

1. Crystal structure of new selenosilicates Pb$_{1,75}$M$_{0,5}$SiSe$_4$ (M = Cu and Ag) / L. D Gulay, M. R. Huch, M. Wołcyrz, I. D Olekseyuk // J. Alloys Compds. – 2005. – Vol. 402. – P. 115–117.
2. Hahn H. Über einige ternare Chalkogenide vom Argyrodit-Typ / H. Hahn, H. Schulze, J. Sechsev // Naturwis. – 1965. – H. 52. – S. 451.
3. Iglesias J. E. Ternary chalcogenide compounds AB$_2$X$_4$ / J. E. Iglesias, H. Steinfink // J. Solid State Chem. – 1973. – Vol. 6, № 1. – P. 93–98.
4. Investigation of the Pr$_2$Se$_3$–Cu$_2$Se–PbSe and Pr$_2$Se$_3$–Ag$_2$Se–PbSe systems / O. V. Marchuk, L. D. Gulay, V. Ya. Shemet, I. D. Olekseyuk // J. Alloys Compds. – 2006. – Vol. 416. – P. 106–109.
5. Iyer R. G. Noncentrosymmetric cubic thio- and selenogermanates: A$_{0,5}$M$_{1,75}$GeQ$_4$ (A = Ag, Cu, Na; M = Pb, Eu; Q = S, Se) / R. G. Iyer, J. A. Aitken, M. G. Kanatzidis // Solid State Sci. – 2004. – Vol. 6. – P. 451–459.
6. Olekseyuk I. D. Phase equilibria in the systems Cu$_2$SiSe$_3$(Te$_3$)–CdSe(Te) / I. D. Olekseyuk, L. V. Piskach, O. V. Parasyuk // Zhurn. Neorgan. Chem. – 1998. – Vol. 43, № 3. – P. 527–530.
7. Peters J. Silicon Disulphide and Silicon Diselenide: A Reinvestigation / J. Peters, B. Krebs // Acta Crystallogr. B. – 1982. – Vol. 38. – P. 1270–1272.
8. Phase equilibria in the systems Ag(Cu)$_2$X–PbX–Ge(Si,Sn)X$_2$ (X = S, Se) / S. I. Levkovets, Y. M. Kogut, L. V. Piskach, O. V. Parasyuk // XVIII Ukrainian Conference on Inorganic Chemistry, Book of Abstracts. – Kharkiv, 2011. – P. 179.
9. Rivet J. Contribution a l'etude de quelques combinaisons ternaires sulfurees, seleniees ou tellurees du cuivre avec les elements du groupe IV b / J. Rivet // Ann. Chim. – 1965. – Vol. 10, № 5–6. – P. 243–270.
10. Use of the CSD program package for structure determination from powder data / L. G. Akselrud, P. Yu. Zavalij, Yu. M. Grin' et al. // Mat. Sci. Forum. – 1993. – Vol. 133. – P. 335–340.

Шпак Оксана, Когут Юрій, Федорчук Анатолій, Піскач Людмила, Парасюк Олег. Система Cu$_2$Se–PbSe–SiSe$_2$ і кристалічна структура CuPb$_{1,5}$SiSe$_4$. Використовуючи результати рентгенофазового аналізу, побудовано ізотермічний переріз системи Cu$_2$Se–PbSe–SiSe$_2$ при кімнатній температурі. Підтверджено існування тетрарної сполуки та уточнено її склад як CuPb$_{1,5}$SiSe$_4$. Рентгенівським методом порошку уточнено кристалічну структуру CuPb$_{1,5}$SiSe$_4$ (ПГ $I\overline{4}3d$, $a = 1{,}43386$ нм, $R_I = 0{,}0834$).

Ключові слова: ізотермічний переріз, кристалічна структура, халькогеніди.

Шпак Оксана, Когут Юрий, Федорчук Анатолий, Пискач Людмила, Парасюк Олег. Система Cu$_2$Se–PbSe–SiSe$_2$ и кристаллическая структура CuPb$_{1,5}$SiSe$_4$. Используя результаты рентгенофазового анализа, было построено изотермическое сечение системы Cu$_2$Se–PbSe–SiSe$_2$ при комнатной температуре. Подтверждено существование тетрарного соединения и уточнено его состав как CuPb$_{1,5}$SiSe$_4$. Рентгеновским методом порошка уточнена кристаллическая структура CuPb$_{1,5}$SiSe$_4$ (ПГ $I\overline{4}3d$, $a = 1{,}43386$ нм, $R_I = 0{,}0834$).

Ключевые слова: изотермическое сечение, кристаллическая структура, халькогениды.

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Про доцільність реверсування напряму струму при одержанні порошків цинк оксиду методом електрохімічного осадження

Показано можливість отримання нанокристалів цинк оксиду електрохімічним методом з використанням цинкових електродів і реверсування напряму постійного струму. Реверсування напряму струму дає можливість забезпечити рівномірне використання цинкових електродів і постійне значення сили струму. Синтез при використанні змінного струму має низький вихід і одержується суміш кристалічного та аморфного продуктів. Отримані порошки досліджено за допомогою таких методів, як рентгенофазовий аналіз та скануюча електронна мікроскопія.

Ключові слова: цинк оксид, електрохімічне осадження, зміна напряму струму.